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RESIN COATING COMPOSITION AND METHOD OF CURING IT

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Abstract

Problem

To provide a resin coating composition with excellent smoothness, water repellency, and mold releasability and a method of curing the same.

Means to solve

A resin coating composition is produced by reacting a polyurethane resin derivative that has polydimethylsiloxane side chains and isocyanate groups in the main polyurethane molecular chain with a hydroxyl group-containing resin. The resin coating composition is cured by thermal crosslinking after adding polyisocyanate with at least two isocyanate groups per molecule to this resin coating composition.

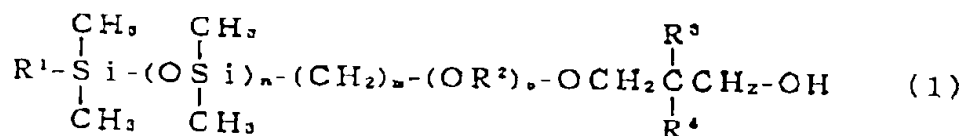
Claims

1. A resin coating composition obtained by reacting a polyurethane resin derivative that has polydimethylsiloxane side chains and isocyanate groups in the main polyurethane molecular chain with a hydroxyl group-containing resin.

2. The resin coating composition of Claim 1 wherein the polyurethane resin derivative is obtained by reacting (A) a polydimethylsiloxane that has an alkyl group at one end and two hydroxyl groups at the other end with (B) a polyisocyanate that has at least two isocyanate groups in the molecule as the essential components.

3. The resin coating composition of Claim 2 wherein the polydimethylsiloxane of (A) is polydimethylsiloxane represented by the following general formula (1)

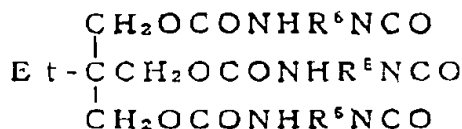
[Structure 1]



(wherein R¹ is an alkyl group having 1 to 4 carbon atoms, R² is an ethylene or propylene group, R³ is a hydrogen, methyl group, or ethyl group, R⁴ is a hydroxyl or methylhydroxyl group, n is an integer of 0-100, p is an integer of 0-100, and m is an integer of 2-9).

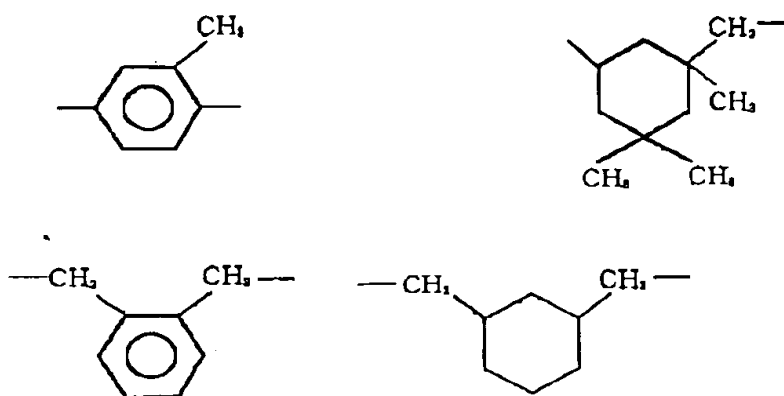
4. The resin coating composition of Claims 2 or 3 wherein the polyisocyanate of (B) is a polyisocyanate represented by the following general formula (2)

[Structure 2]



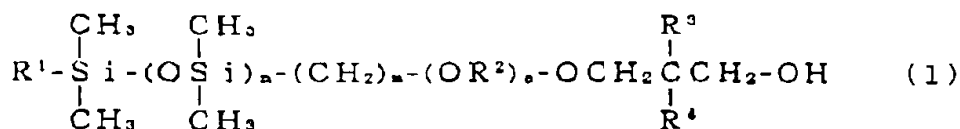
(wherein Et is an ethyl group and R⁵ is -(CH₂)₆- or

[Structure 3]



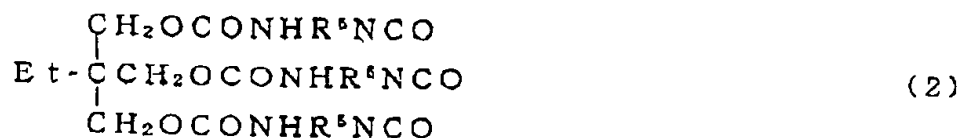
6. [sic] The resin coating composition of Claim 1 wherein the polyurethane resin derivative is obtained by reacting a polydimethylsiloxane represented by the following general formula (1)

[Structure 4]



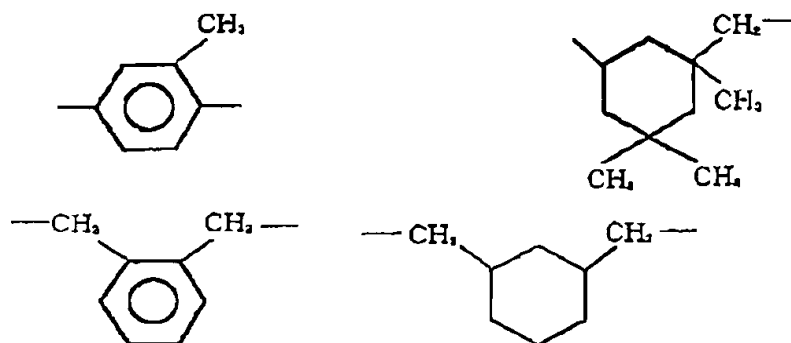
(wherein R^1 is an alkyl group having 1 to 4 carbon atoms, R^2 is an ethylene or propylene group, R^3 is a hydrogen, methyl group, or ethyl group, R^4 is a hydroxyl or methylhydroxyl group, n is an integer of 0-100, p is an integer of 0-100, and m is an integer of 2-9) with a polyisocyanate represented by the following general formula (2)

[Structure 5]



(wherein Et is an ethyl group and R^5 is $-(\text{CH}_2)_6-$ or

[Structure 6]



in a molar ratio of 1:6:1 to 1:10.)

7. The resin coating composition of any of Claims 1-6 wherein the hydroxyl group-containing resin is an acrylic polyol, fluorine-containing polyol, polyoxyalkylene, polyester polyol, polyvinyl alcohol, or a mixture of two or more thereof.

8. The resin coating composition of any of Claims 1-7 wherein the mixture ratio in the reaction of the hydroxyl group-containing resin and the polyurethane resin derivative is 0.1-10 mol% of isocyanate groups in the polyurethane resin derivative based on the hydroxyl groups in the hydroxyl group-containing resin.

9. A resin coating composition obtained by mixing a hydroxyl group-containing resin with the product of the reaction of a polyurethane resin derivative that has polydimethylsiloxane side chains and isocyanate groups in the main polyurethane molecular chain and a polyoxyalkylene with one hydroxyl group in the molecule.

10. The resin coating composition of Claim 9 wherein the hydroxyl group-containing resin is an acrylic polyol, fluorine-containing polyol, polyoxyalkylene, polyester polyol, polyvinyl alcohol, or a mixture of two or more thereof.

11. A method of curing a resin coating composition that consists of crosslinking by adding a polyisocyanate with at least two isocyanate groups per molecule to any of the resin coating composition of Claims 1-10.

12. The method of curing a resin coating composition of Claim 11 wherein the mixture ratio of resin coating composition and polyisocyanate resin is 0.3-2.0 mol of isocyanate groups in the polyisocyanate per 1 mol of hydroxyl groups in the resin coating composition.

Detailed explanation of the invention

[0001]

Technical field of the invention

The present invention relates to a dimethylsiloxane-modified urethane resin coating composition that has excellent mold releasability, smoothness, and water repellency.

[0002]

Prior art

Resins with hydroxyl groups in the molecule are often used as paint binders, ink bases, adhesives, and coatings because of their excellent flexibility, adhesiveness, film-forming property, and pigment dispersivity. However, the addition of silicone to the hydroxyl group-containing resin is being studied to impart mold releasability, smoothness, and water repellency in addition to the aforementioned properties.

[0003]

However, when a silicone such as dimethylsiloxane is added to a hydroxyl group-containing resin, the film formed by application of the resin with added silicone becomes opaque and the surface lacks smoothness due to the poor compatibility of the silicone and resin. Furthermore, since the silicone and the aforementioned resin do not bond chemically even if the compatibility can be improved, the silicone bleeds out over time and it becomes impossible to attain the initial goals.

[0004]

Hydroxyl group-containing resins that are chemically modified by silicone have been proposed to solve the aforementioned problems and to make the effects of silicone addition persistent. Specifically, silicone is grafted to the hydroxyl groups in the resin by using reactive silicone containing organic functional groups that react with hydroxyl groups such as those in carboxyl and epoxy groups. However, the low reactivity makes this method impractical because large amounts of unreacted silicone remain in the reaction mixture.

[0005]

Problems to be solved by the invention

As a result of studies conducted to solve the aforementioned problems, the present inventors attained the present invention by discovering that polydimethylsiloxane can be incorporated into hydroxyl group-containing resins as a result of copolymerization when a polyurethane resin derivative that has polydimethylsiloxane side chains and isocyanate groups is reacted with a hydroxyl group-containing resin and that the resin coating composition obtained in this way reacts easily with polyisocyanate and forms a coating film with excellent water repellency, mold releasability, and smoothness. Therefore, a resin coating composition that solves the aforementioned problems and a method of curing it are provided to meet these goals.

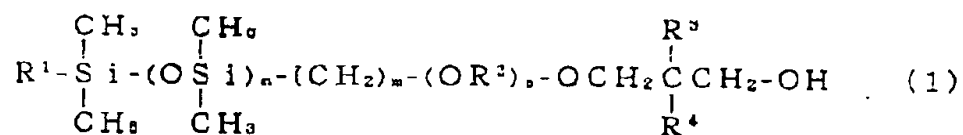
[0006]

Means to solve the problems

To attain the aforementioned goals, the present invention [1] proposes a resin coating composition obtained by reacting a polyurethane resin derivative that has polydimethylsiloxane side chains and isocyanate groups in the main polyurethane molecular chain with a hydroxyl group-containing resin and includes [2] the polyurethane resin derivative being obtained by reacting (A) a polydimethylsiloxane that has an alkyl group at one end and two hydroxyl groups at the other end and (B) a polyisocyanate that has at least two isocyanate groups in the molecule as the essential components, [3] the polydimethylsiloxane of (A) being a polydimethylsiloxane represented by the following general formula (1)

[0007]

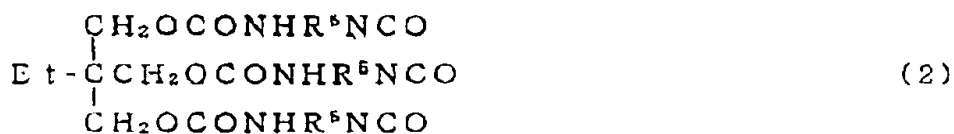
[Structure 7]



(wherein R¹ is an alkyl group having 1 to 4 carbon atoms, R² is an ethylene or propylene group, R³ is a hydrogen, methyl group, or ethyl group, R⁴ is a hydroxyl or methylhydroxyl group, n is an integer of 0-100, p is an integer of 0-100, and m is an integer of 2-9), [4] the polyisocyanate of (B) being a polyisocyanate represented by the following general formula (2)

[0008]

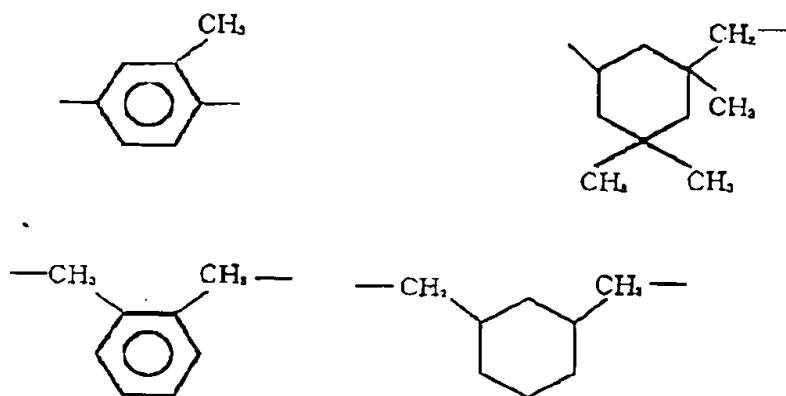
[Structure 8]



(wherein Et is an ethyl group and R⁵ is -(CH₂)₆- or

[0009]

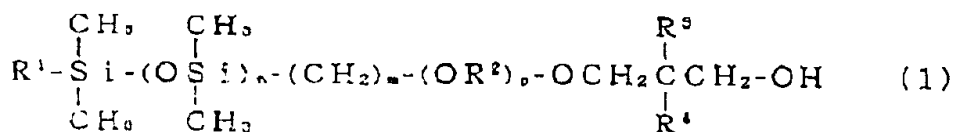
[Structure 9]



[5] the polyurethane resin derivative being obtained by reacting a polydimethylsiloxane represented by the following general formula (1)

[0010]

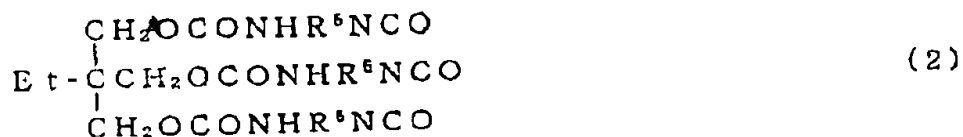
[Structure 10]



(wherein R^1 is an alkyl group having 1 to 4 carbon atoms, R^2 is an ethylene or propylene group, R^3 is a hydrogen, methyl group, or ethyl group, R^4 is a hydroxyl or methylhydroxyl group, n is an integer of 0-100, p is an integer of 0-100, and m is an integer of 2-9) with a polyisocyanate represented by the following general formula (2)

[0011]

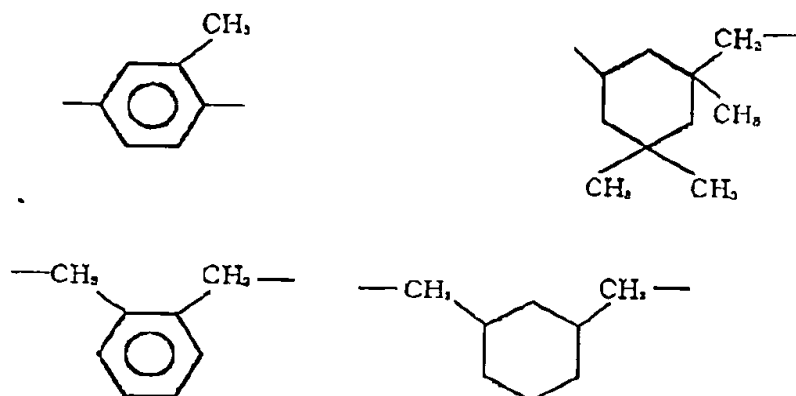
[Structure 11]



(wherein Et is an ethyl group and R^5 is $-(\text{CH}_2)_6-$ or

[0012]

[Structure 12]



in a molar ratio of 1.6:1 to 1:10), [7] the hydroxyl group-containing resin being an acrylic polyol, fluorine-containing polyol, polyoxyalkylene, polyester polyol, polyvinyl alcohol, or a mixture of two or more thereof, and [8] the mixture ratio of the hydroxyl group-containing resin and polyurethane resin derivative in the reaction being 0.1-10 mol% of isocyanate groups in the polyurethane resin derivative based on the hydroxyl groups in the hydroxyl group-containing resin.

[0013]

The present invention also includes [9] a method for curing a resin coating composition wherein crosslinking is performed by adding polyisocyanate that has at least two isocyanate groups per molecule to the resin coating composition of any of [1]-[8] above and [10] the mixture ratio of the resin coating composition and polyisocyanate resin being 0.3-2.0 mol of isocyanate groups in the polyisocyanate per 1 mol of hydroxyl groups in the resin coating composition.

[0014]

The present invention is explained in detail below.

[0015]

Practical embodiment of the invention

The resin coating composition of the present invention is obtained by reacting a polyurethane resin derivative that has polydimethylsiloxane side chains and isocyanate groups in the main polyurethane molecular chain with a hydroxyl group-containing resin.

[0016]

The chemical structure of the aforementioned polyurethane resin derivative consists primarily of the main chain made up of polyurethane molecules, polydimethylsiloxane side chains bonded to the aforementioned main chain, and isocyanate groups bonded to the aforementioned main chain.

[0017]

The aforementioned polyurethane resin derivative can be manufactured by a process such as reacting (A) a polydimethylsiloxane that has an alkyl group at one end and two hydroxyl groups at the other end with (B) a polyisocyanate that has at least three [sic; two] isocyanate groups in the molecule.

[0018]

Since the aforementioned polyurethane resin derivative contains highly reactive isocyanate groups in the molecule, they can be utilized to modify the polyurethane resin derivative with compounds that have various functional groups. Therefore, addition of this polyurethane resin derivative can impart different properties by modification in addition to the inherent properties of the silicone and polyurethane and thus provide a wider range of possible uses.

[0019]

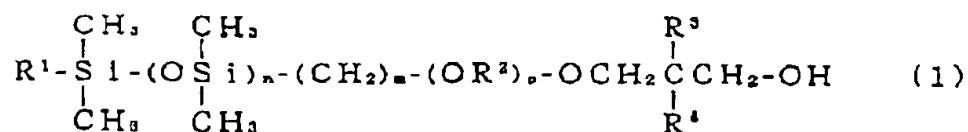
The aforementioned polyurethane resin derivative can also self-crosslink. Therefore, it can also be used appropriately for conventional uses such as paints, sealants, and adhesives.

[0020]

Compounds represented by the following general formula (1) are preferred as the polydimethylsiloxane that has an alkyl group at one end and two hydroxyl groups at the other end of (A).

[0021]

[Structure 13]



In general formula (1), R¹ is an alkyl group having 1 to 4 carbon atoms such as a methyl, ethyl, propyl, or butyl group. A butyl group is especially preferred.

[0022]

R² is an ethylene or propylene group. An ethylene group is especially preferred.

[0023]

R³ is hydrogen, a methyl group, or ethyl group. Hydrogen is especially preferred.

[0024]

R⁴ is a hydroxyl or methylhydroxyl group. A methylhydroxyl group is especially preferred.

[0025]

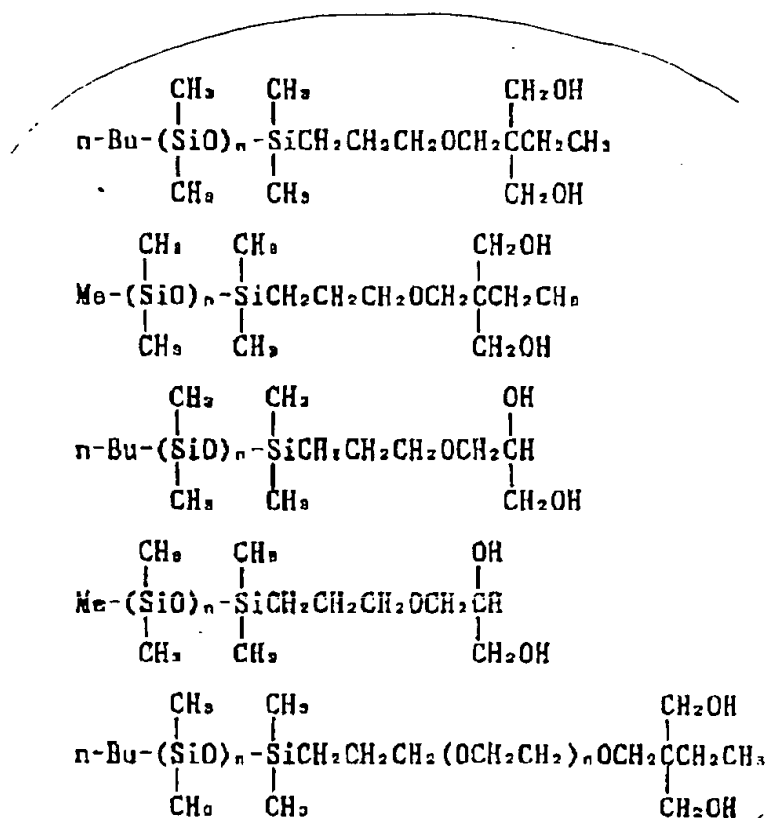
n is an integer of 0-100, p is an integer of 0-100, and m is an integer of 2-9.

[0026]

Concrete examples of the polydimethylsiloxane of (A) include

[0027]

[Structure 14]

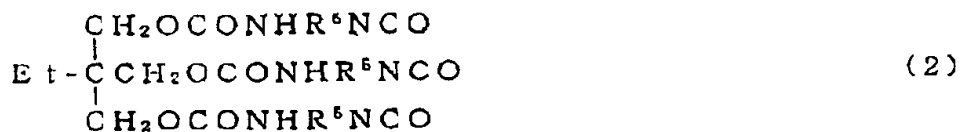


[0028]

Compounds represented by the following general formula (2) are preferred as the polyisocyanate that has at least three isocyanate groups in the molecule of (B).

[0029]

[Structure 15]



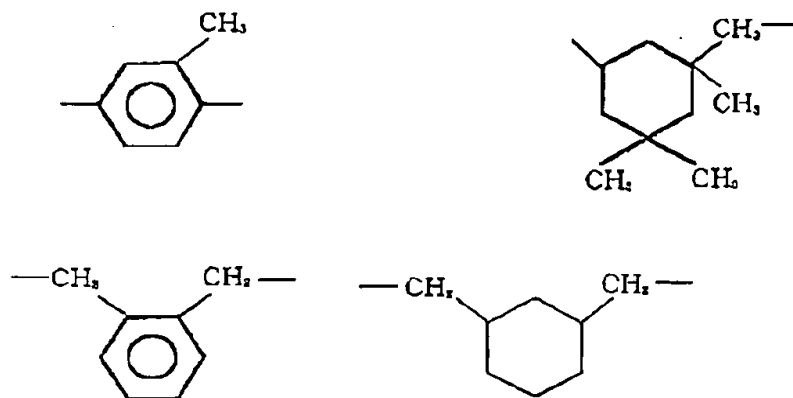
In general formula (2), Et is an ethyl group.

[0030]

R⁵ is -(CH₂)₆- or

[0031]

[Structure 16]



[0032]

The mixture ratio in the reaction of the aforementioned polydimethylsiloxane of (A) and polyisocyanate of (B) is preferably 1.05-15 Eq of isocyanate groups in the polyisocyanate of (B) based on the hydroxyl groups in the polydimethylsiloxane of (A).

[0033]

A polyurethane resin derivative manufactured by reacting a polydimethylsiloxane of general formula (1) and a polyisocyanate of general formula (2) is especially preferred in the present invention. The polydimethylsiloxane of general formula (1) and polyisocyanate of general formula (2) are preferably reacted at a molar ratio of 1.4:1 to 1:10 in this reaction.

[0034]

When the molar ratio of the polydimethylsiloxane of (1) exceeds the aforementioned value, the few isocyanate groups that remain in the urethane resin reduce the working effects that are the goal of the present invention. Not all of the hydroxyl groups and all of the isocyanate groups need necessarily react completely in the present invention. Therefore, unreacted isocyanate groups remain in the urethane molecule produced even when an excess of hydroxyl groups has been combined.

[0035]

When the molar ratio of the polyisocyanate of (2) exceeds the aforementioned value, unreacted polyisocyanate of (2) remains. However, a ratio of no more than 1:3 is preferred for uses in which residual polyisocyanate has a negative effect.

[0036]

No special reaction equipment or conditions need be used to produce the aforementioned polyurethane resin derivative.

[0037]

Although a solvent need not be used in the aforementioned reaction, it is preferable to employ one. Examples of solvents that can be used include esters such as methyl acetate, ethyl acetate, and butyl acetate, ketones such as acetone and methyl ethyl ketone, aromatic hydrocarbons such as toluene and xylene, and ethers such as diethyl ether, dibutyl ether, tetrahydrofuran, and dioxane. These can be used individually or in mixtures of two or more types.

[0038]

Use of a catalyst is optional. Known catalysts commonly used in the production of urethane resin can be used individually or in combinations of two or more types. Concrete examples include organotin compounds such as dibutyltin dilaurate and tin dioctoate and tertiary amines such as triethylamine, N-ethylmorpholine, and 1,8-diazabicyclo[5.4.0]undecene-7.

[0039]

The amount of catalyst used is 0.001-20 wt%, preferably 0.01-1.0 wt%, based on the polyurethane resin derivative.

[0040]

The reaction temperature is preferably from room temperature to 150°C, especially 50-120°C. The duration of the reaction varies depending on whether a catalyst is used, but is usually 1-20 h.

[0041]

The aforementioned polyurethane resin derivative produced as described above is given highly reactive isocyanate groups and dimethylsiloxane as molecular side chains.

[0042]

This polyurethane resin derivative can be chemically modified and is also capable of self-crosslinking. Any compounds that have functional groups that react with conventional isocyanate groups can be used when further modifying the polyurethane derivative by reaction

with said isocyanate groups. Examples of compounds that contain active hydrogens used in modification include alcohols, carboxylic acids, amines, ureas, and urethanes.

[0043]

The resin coating composition of the present invention is obtained by reacting the polyurethane resin derivative obtained by the aforementioned method with a hydroxyl group-containing resin.

[0044]

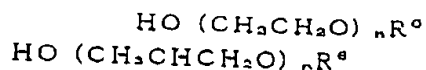
Any resin can be used as the hydroxyl group-containing resin to be reacted with the aforementioned polyurethane resin derivative as long as it has at least one hydroxyl group in the molecule. Hydroxyl group-containing resins that have one hydroxyl group in the molecule and hydroxyl group-containing resins that have two or more hydroxyl groups in the molecule are each important in the present invention because they impart different properties to the resin coating obtained, as will be discussed below.

[0045]

Compounds represented by the following formulas are preferred as hydroxyl group-containing resins that have one hydroxyl group in the molecule.

[0046]

[Structure 17]



wherein R^a is a hydrocarbon having 1 to 18 carbon atoms or a functional group with unsaturated bonds such as vinyl, allyl, or methacryl. Any can be used as long as it is readily available in industrial practice. Polyoxyethylene in which R^a is any group with relatively few carbon atoms such as methyl, ethyl, propyl, vinyl, or allyl is preferred for the high compatibilizing effect discussed below. n is preferably 1-500, more preferably 10-200 from the standpoint of compatibility.

[0047]

The resin coating composition of the present invention, obtained by reacting the polyurethane resin derivative and hydroxyl group-containing resin with one hydroxyl group in the molecule such as the aforementioned polyoxyalkylene, is used mixed with a hydroxyl

group-containing resin for paint as described below. It is obtained by reacting the amount of polyoxyalkylene that consumes at least 10%, preferably 100%, of the isocyanate groups bonded to the polyurethane resin derivative with the polyurethane resin derivative.

[0048]

The resin coating composition obtained in this way has good compatibility with hydroxyl group-containing resins for paint such as fluorine-containing polyols, polyoxyalkylenes, polyvinyl alcohols, acrylic polyols, polyester polyols, and polyurethane polyols. Therefore, the coating composition obtained by reacting the polyurethane resin derivative and hydroxyl group-containing resin with one hydroxyl group in the molecule such as the aforementioned polyoxyalkylene produces a transparent solution when merely mixed with the aforementioned solution of resin for paint. This solution is preferred as the resin coating composition of the present invention. A silicone-modified coating with excellent transparency can be obtained merely by adding polyisocyanate as a curing agent to the solution and heating.

[0049]

Even though the compound produced by the crosslinking reaction with polyisocyanate in this case is a hydroxyl group-containing resin for paint, the coating film of this product does not bleed due to the extremely good compatibility between the coating composition, obtained by reacting the polyurethane resin derivative and hydroxyl group-containing resin with one hydroxyl group in the molecule, and the aforementioned hydroxyl group-containing resin for paint.

[0050]

On the other hand, the hydroxyl group-containing resin with at least two hydroxyl groups preferably has a hydroxyl value of 10-400, especially 15-250. This value represents the hydroxyl value of the solution when the hydroxyl group-containing resin is dissolved in a conventional solvent. The Gardner viscosity is preferably C-Z. The solution can be used diluted when the viscosity is higher. Adjustment to a Gardner viscosity of F-V is especially preferred for coating.

[0051]

Concrete examples of such resins are acrylic polyols such as Acrylic A-801 and A-814 made by Dainippon Ink and Chemicals, Takelac UA-702 and UA-902 made by Takeda Chemical Industries, and Hitaloid [transliteration] 3008 and 3004 made by Hitachi Kasei Kogyo.

[0052]

Examples of polyester polyols include Takelac U-24 and U-27 made by Takeda Chemical Industries.

[0053]

Examples of fluorine-containing polyols include Lumiflon LF-400 and LF-600 made by Asahi Glass.

[0054]

Other examples include polyoxyalkylenes such as polyethylene glycol and polypropylene glycol, polyvinyl alcohol, and polyurethane polyol.

[0055]

The mixture ratio in the reaction of hydroxyl group-containing resin with at least two hydroxyl groups and polyurethane resin derivative is preferably such that there is no more than 10 mol% of isocyanate groups in the polyurethane resin derivative based on hydroxyl groups in the hydroxyl group-containing resin. There is a danger that gelation will occur during the reaction or during the storage of the resin coating composition obtained when the ratio exceeds 10 mol% due to the numerous isocyanate groups present in the polyurethane resin derivative. An aforementioned ratio of less than 0.1 mol% gives a low percentage of polydimethylsiloxane incorporated into the hydroxyl group-containing resin. This decreases the properties such as water repellency. Therefore, the aforementioned ratio is preferably 10-0.1 mol%.

[0056]

The reaction of the polyurethane resin derivative and hydroxyl group-containing resin that has one or two or more hydroxyl groups in the molecule does not require any special reaction equipment or conditions. The reaction is conducted using equipment and conditions that are known to persons in the industry.

[0057]

It is preferable to use a solvent when conducting the reaction. Examples of solvents that can be used include esters such as methyl acetate, ethyl acetate, and butyl acetate, ketones such as acetone and methyl ethyl ketone, aromatic hydrocarbons such as toluene and xylene, and ethers such as diethyl ether, dibutyl ether, tetrahydrofuran, and dioxane. These solvents can be used individually or in mixtures of two or more types.

[0058]

A catalyst may or may not be used. Those commonly used in the production of urethane resins are preferred. Examples include organotin compounds such as dibutyltin dilaurate and tin dioctoate and tertiary amines such as triethylamine, N-ethylmorpholine, and 1,8-diazobicyclo[5.4.0]undecene-7. The catalysts may be used individually or in combinations of two or more types. The amount of catalyst used is 0.001-20 wt%, preferably 0.01-1.0 wt%, based on the polyurethane resin derivative.

[0059]

The reaction temperature is preferably from room temperature to 150°C, especially 50-120°C.

[0060]

The duration of the reaction varies depending on whether or not a catalyst is used. The reaction is usually completed in 1 to 20 h.

[0061]

The resin coating composition of the present invention obtained by the reaction of the polyurethane resin derivative and hydroxyl group-containing resin can be cured by using a polyisocyanate that contains at least two isocyanate groups per molecule as the curing agent.

[0062]

Examples of the curing agent include known diisocyanates commonly used in polyurethane resins such as 2,4-tolylene diisocyanate, 2,6-tolylene diisocyanate, m-phenylene diisocyanate, p-phenylene diisocyanate, and 4,4'-diphenylmethane diisocyanate and addition products of these organic isocyanates and other compounds, e.g., a polyisocyanate represented by the aforementioned general formula (2). However, the curing agents are not limited to these.

[0063]

The mixture ratio of the resin coating composition of the present invention and the curing agent is preferably 0.3-2.0 Eq of isocyanate groups in the polyisocyanate based on the hydroxyl groups in the resin coating composition.

[0064]

Conventional curing conditions for urethane coatings are sufficient to cure this resin coating composition by a curing agent. Concretely speaking, it can be cured by allowing it to

stand for several days open to the air or under controlled humidity or for several min to several h by heating at 50-150°C. These curing conditions can be used, for example, to cure the composition at room temperature when it is applied to the outer walls of buildings or to cure the composition in 1-2 min at around 100°C on steel plate priming lines when priming steel plates.

[0065]

The resin coating composition of the present invention makes it possible to form a coating film with desirable properties such as water repellency, mold releasability, and smoothness on the surface of various objects to be coated by applying the composition mixed with the curing agent as is and followed by curing by heating.

[0066]

The resin coating composition of the present invention can also be utilized in paints, etc. by mixing it with pigments, dyes, and other fillers.

[0067]

The present invention is explained concretely below through Application Examples.

[0068]

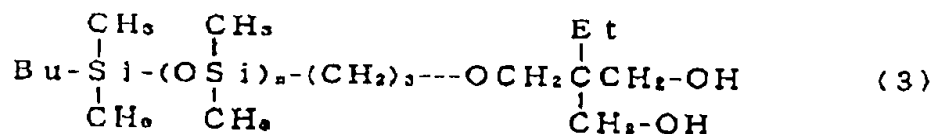
Application Examples

Polyurethane resin derivative, Production Example 1

13.9 g (0.02 mol hydroxyl groups) of a single-end diol-modified silicone with a hydroxyl value of 670 represented by the following formula (3),

[0069]

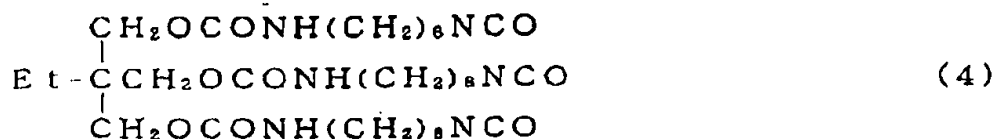
[Structure 18]



10.0 g (0.03 mol isocyanate) of polyisocyanate (Takenate DI60N made by Takeda Chemical Industries) with 333.3 NCO Eq and a solids fraction concentration of 75 wt% represented by formula (4) below,

[0070]

[Structure 19]



and 40 g of toluene were placed in a 100-mL flask and stirred while heating for 22 h at 80°C.

[0071]

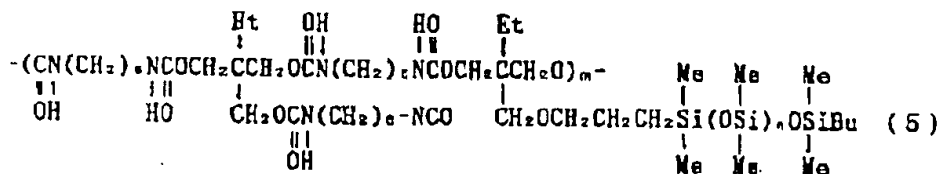
Figure 1 shows the GPC (gel permeation chromatography, eluant: toluene) graphs with heating and stirring times of 0 and 22 h. Figure 1 confirms essentially complete consumption of the silicone.

[0072]

Figure 2 shows an IR graph of the reaction composition after heating and stirring for 22 h. The IR graph confirms that the reaction composition contains isocyanate and dimethylsilicone. These analytical results demonstrate that the composition obtained by this reaction is a polyurethane resin derivative represented by the following formula (5).

[0073]

[Structure 20]

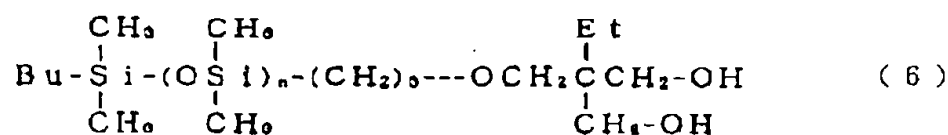


Polyurethane resin derivative, Production Example 2

15.0 g (0.0067 mol hydroxyl groups) of a single-end diol-modified silicone with a hydroxyl value of 2240 represented by the following formula (6),

[0074]

[Structure 21]



3.4 g (0.01 mol isocyanate) of polyisocyanate (Takanate D160N made by Takeda Chemical Industries), 40 g of toluene, and 0.2 g of a 1 wt% toluene solution of dibutyltin dilaurate were placed in a 100-mL flask and stirred while heating for 4 h at 80°C.

[0075]

Figure 3 shows the GPC (eluant: toluene) graphs with heating and stirring times of 0 and 4 h. Figure 3 confirms that essentially all of the silicone was consumed after heating and stirring for 4 h.

[0076]

Figure 4 shows the IR graph of the product obtained after heating and stirring for 4 h. The IR graph of Figure 4 confirms that the products obtained after the reaction contain isocyanate.

[0077]

Polyurethane resin derivative, Production Example 3

0.32 g (0.005 mol hydroxyl groups) of a single-end diol-modified silicone with a hydroxyl value of 670, 3.2 g (0.08 mol isocyanate) of polyisocyanate (Takenate D140N made by Takeda Chemical Industries) with 400 NCO Eq and a solids fraction concentration of 75 wt%, 6.5 g of toluene, and 4 g of xylene were placed in a flask. A polyurethane resin derivative was obtained by heating and stirring for 1 hour at 80°C.

[0078]

Polyurethane resin derivative, Production Example 4

0.34 g (0.00005 mol hydroxyl groups) of a single-end diol-modified silicone with a hydroxyl value of 6040, 3.2 g (0.08 mol isocyanate) of polyisocyanate (Takenate D140N made by Takeda Chemical Industries) with 400 NCO Eq and a solids fraction concentration of 75 wt%, 6.5 g of toluene, and 4 g of xylene were placed in a 50-mL flask. A polyurethane resin derivative was obtained by heating and stirring for 1 hour at 80°C.

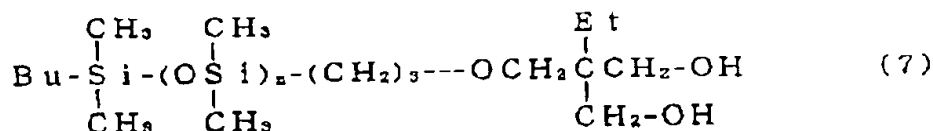
[0079]

Polyurethane resin derivative, Production Example 5

18.9 g (0.02 mol hydroxyl groups) of a single-end diol-modified silicone with a hydroxyl value of 670 represented by the following formula (7),

[0080]

[Structure 22]



18.3 g (0.04 mol isocyanate) of polyisocyanate (Takenate DI60N), 51 g of toluene, and 0.2 g of a 1 wt% toluene solution of dibutyltin dilaurate were placed in a 100-mL flask and heated and stirred for 8 h at 80°C.

[0081]

The results of GPC (eluant: toluene) and IR measurement after 3 h showed that essentially all of the silicone had been consumed after heating and stirring for 3 h and that the product obtained contained isocyanate and dimethylsilicone.

[0082]

Application Example 1

8.4 g (0.0014 mol isocyanate) of the polyurethane resin derivative obtained in Production Example 1, 50 g (0.05 mol hydroxyl groups) of acrylic polyol (A-801, made by Dainippon Ink and Chemicals, nonvolatile fraction 50 wt%, hydroxyl group concentration 0.001 mol/g), 7 g of toluene, and 0.3 g of a 1 wt% toluene solution of dibutyltin dilaurate were placed in a 200-mL flask and stirred while heating for 5 h at 90°C to obtain a resin coating composition. Figures 5 and 6 show the IR spectra before and after heating and stirring. The disappearance of the peak attributed to isocyanate after heating and stirring confirmed the end of the reaction.

[0083]

The resin coating composition obtained was stable with no changes in viscosity even after more than 1 month at normal temperature.

[0084]

Next, 10.0 g (0.0074 mol hydroxyl groups) of the aforementioned resin coating composition and 2.71 g (0.0081 mol isocyanate) of polyisocyanate (DI60N) were mixed, applied at a thickness of 20 μm to a soft steel plate, dried for 10 min, then heated for 2 h at 80°C.

[0085]

The coating obtained had the following properties.

[0086]

[Table 1]

Table 1

Contact angle with water: 98°
Pencil hardness: HB (damage) 3H (breakage)
Bendability: No abnormality at 2 mm
Checkerboard test: 100/100
Rubbing test (xylene): <1 μm reduction in film after 100 times
Film transparency: Somewhat cloudy

Application Example 2

8.4 g (0.0006 mol isocyanate) of the polyurethane resin derivative obtained in Production Example 1, 30 g (0.03 mol hydroxyl groups) of acrylic polyol (A-801, made by Dainippon Ink and Chemicals, nonvolatile fraction 50 wt%, hydroxyl group concentration 0.001 mol/g), 7 g of toluene, and 0.1 g of a 1 wt% of toluene solution of dibutyltin dilaurate were placed in a 200-mL flask and stirred while heating for 3 h at 90°C. The reaction mixture obtained was stable with no change in viscosity even after more than 1 month.

[0087]

Next, 15.0 g (0.01 mol hydroxyl groups) of the aforementioned reaction mixture and 3.8 g (0.011 mol isocyanate) of polyisocyanate (DI60N) were mixed, applied at a thickness of 16 μm to a soft steel plate, dried for 10 min, then heated for 2 h at 80°C.

[0088]

The coating obtained had the following properties.

[0089]

[Table 2]

Table 2

Contact angle with water: 98° Pencil hardness: F (damage) 4H (breakage) Bendability: No abnormality at 2 mm Checkerboard test: 100/100 Rubbing test (xylene): No reduction in film after 100 times Film transparency: Somewhat cloudy
--

Application Example 3

1.07 g (0.00006 mol isocyanate) of the polyurethane resin derivative obtained in Production Example 2, 30 g (0.03 mol hydroxyl groups) of acrylic polyol (A-801, made by Dainippon Ink and Chemicals, nonvolatile fraction 50 wt%, hydroxyl group concentration 0.001 mol/g), and 12.7 g of toluene were placed in a 100 mL flask and stirred while heating for 5 h at 90°C. The resin coating composition obtained was stable with no change in viscosity even after 1 month.

[0090]

Next, 15.0 g (0.01 mol hydroxyl groups) of the aforementioned resin coating composition and 3.8 g (0.011 mol isocyanate) of polyisocyanate (D160N) were mixed, applied at a thickness of 15 μm to a soft steel plate, dried for 10 min, then heated for 2 h at 80°C.

[0091]

The coating obtained had the following properties.

[0092]

[Table 3]

Table 3

Contact angle with water: 102° Pencil hardness: F (damage) 4H (breakage) Bendability: No abnormality at 2 mm Checkerboard test: 100/100 Rubbing test (xylene): <1 μm reduction in film after 100 times Film transparency: Cloudy
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Application Example 4

The entire amount of the reaction solution obtained in Production Example 3 (0.0075 mol isocyanate) and 7.52 g (0.0072 mol hydroxyl groups) of acrylic polyol (A-801) were mixed, cured for 4 h at room temperature, then applied at a thickness of 6 μm to an aluminum plate. After drying for 10 min, the plate was heated for 2 h at 80°C. The coating film obtained had a contact angle with water of 101° and was transparent.

[0093]

Application Example 5

The entire amount of the resin coating composition obtained in Production Example 4 (0.008 mol isocyanate) and 7.94 g (0.008 mol hydroxyl groups) of acrylic polyol (A-801) were mixed, cured for 3 h at room temperature, then applied at a thickness of 7 μm to an aluminum plate. After drying for 10 min, the plate was heated for 2 h at 80°C. The coating film obtained had a contact angle with water of 105° and was cloudy.

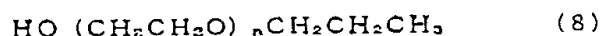
[0094]

Application Example 6

15 g (0.0038 mol isocyanate) of the polyurethane resin derivative obtained in Production Example 5 and 0.85 g (0.0006 mol hydroxyl groups) of polyoxyethylene (hydroxyl Eq = 1470) represented by the following formula (8)

[0095]

[Structure 23]



were placed in a 50 mL flask and stirred while heating for 3 h at 90°C. A resin coating composition was obtained by adding 14.7 g (0.0147 mol hydroxyl groups) of acrylic polyol (A-801) and 6 g of toluene to 5.0 g (0.001 mol isocyanate) of the reaction solution obtained and stirring and heating for 30 min at 90°C.

[0096]

After cooling, 5.0 g (0.015 mol isocyanate) of polyisocyanate (D160N) and 6 g of toluene were mixed with the resin coating composition. The product was applied at a thickness of 15 μm to a soft steel plate, dried for 10 min, then heated for 2 h at 80°C.

[0097]

The coating obtained had the following properties.

[0098]

[Table 4]

Table 4

Contact angle with water: 99°
Pencil hardness: B (damage) 4H (breakage)
Bendability: No abnormality at 2 mm
Checkerboard test: 100/100
Rubbing test (xylene): No reduction in film after 100 times
Film transparency: Transparent

As shown in Table 4, the coating obtained was completely transparent. This confirmed that reacting polyoxyethylene that contains one hydroxyl group in the molecule with the polyurethane resin derivative improves the compatibility with hydroxyl group-containing resins.

[0099]

Application Example 7

15 g (0.0024 mol isocyanate) of the polyurethane resin derivative obtained in Production Example 1, 3.5 g (0.0024 mol hydroxyl groups) of polyoxyethylene (hydroxyl Eq = 1470) represented by the above formula (8), and 0.1 g of a 1 wt% toluene solution of dibutyltin dilaurate were placed in a 50-mL flask and stirred while heating for 4 h at 80°C. 15.0 g (0.017 mol hydroxyl groups) of fluorine-containing polyol (F-600 made by Asahi Glass, hydroxyl Eq = 1900), 5.7 g (0.017 mol isocyanate) of polyisocyanate (D160N), and 10.0 g of xylene were mixed with 4.0 g of the reaction solution obtained, applied at a thickness of 18 μm to a soft steel plate, dried for 10 min, then heated for 2 h at 80°C. The coating obtained had a contact angle with water of 101° and was colorless and transparent.

[0100]

Comparative Example 1 (for comparison with Application Examples 1, 2, 3, and 6)

15 g (0.015 mol hydroxyl groups) of acrylic polyol (A-801, made by Dainippon Ink and Chemicals, nonvolatile fraction 50 wt%, hydroxyl group concentration 0.001 mol/g), 5.5 g (0.017 mol isocyanate) of polyisocyanate (D-160N), 0.05 g of a 1 wt% toluene solution of dibutyltin dilaurate, and 12 g of toluene were mixed, applied at a thickness of 20 μm to a soft

steel plate and dried for 10 min, then heated for 2 h at 80°C. Table 5 shows the properties of the coating obtained.

[0101]

[Table 5]

Table 5

Contact angle with water: 83°
Pencil hardness: HB (damage) 4H (breakage)
Bendability: No abnormality at 2 mm
Checkerboard test: All separated
Rubbing test (xylene): 2 μ m reduction in film after 100 times
Film transparency: Basically transparent

Comparative Example 2 (for comparison with Application Examples 4 and 5)

8 g (0.008 mol hydroxyl groups) of acrylic polyol (A-801), 3.2 g (0.008 mol isocyanate) of polyisocyanate (D-140N), and 4 g of xylene were mixed, applied at a thickness of 7 μ m to an aluminum plate, dried for 10 min, then heated for 2 h at 80°C. The coating obtained had a contact angle with water of 85°.

[0102]

Comparative Example 3 (for comparison with Application Example 7)

15 g (0.017 mol hydroxyl groups) of fluorine-containing polyol (LF-600, hydroxyl group Eq = 1900), 5.7 g (0.017 mol isocyanate) of polyisocyanate (D-160N), and 10 g of xylene were mixed, applied at a thickness of 16 μ m to a soft steel plate, dried for 10 min, then heated for 2 h at 80°C. The coating obtained had a contact angle with water of 84° and was cloudy.

[0103]

Effects of the invention

The resin coating composition of the present invention is produced by reacting a polyurethane resin derivative that has polydimethylsiloxane side chains and isocyanate groups in the main polyurethane molecular chain with a hydroxyl group-containing resin. Therefore, the reaction is simple and can easily be implemented on an industrial scale. The polydimethylsiloxane is also chemically bonded in this resin coating composition. Therefore, polydimethylsiloxane does not bleed out over the long term when the composition is used in coatings, and a good mold releasability, water repellency, and smoothness can be actualized.

Brief description of the figures

Figure 1 is a GPC graph that shows the changes over time in the amount of unreacted single-end diol-modified silicone in the polyurethane resin derivative of Production Example 1.

Figure 2 is an IR graph of the analysis of the reaction solution after 22 h of reaction of the polyurethane resin derivative of Production Example 1.

Figure 3 is a GPC graph that shows the changes over time in the amount of unreacted single-end diol-modified silicone in the polyurethane resin derivative of Production Example 2.

Figure 4 is an IR graph of the analysis of the reaction solution after 4 h of reaction of the polyurethane resin derivative of Production Example 2.

Figure 5 is an IR graph of the raw material mixture prior to the reaction in the production of the resin coating composition of Application Example 1.

Figure 6 is an IR graph of the reaction mixture after the reaction in the production of the resin coating composition of Application Example 1.

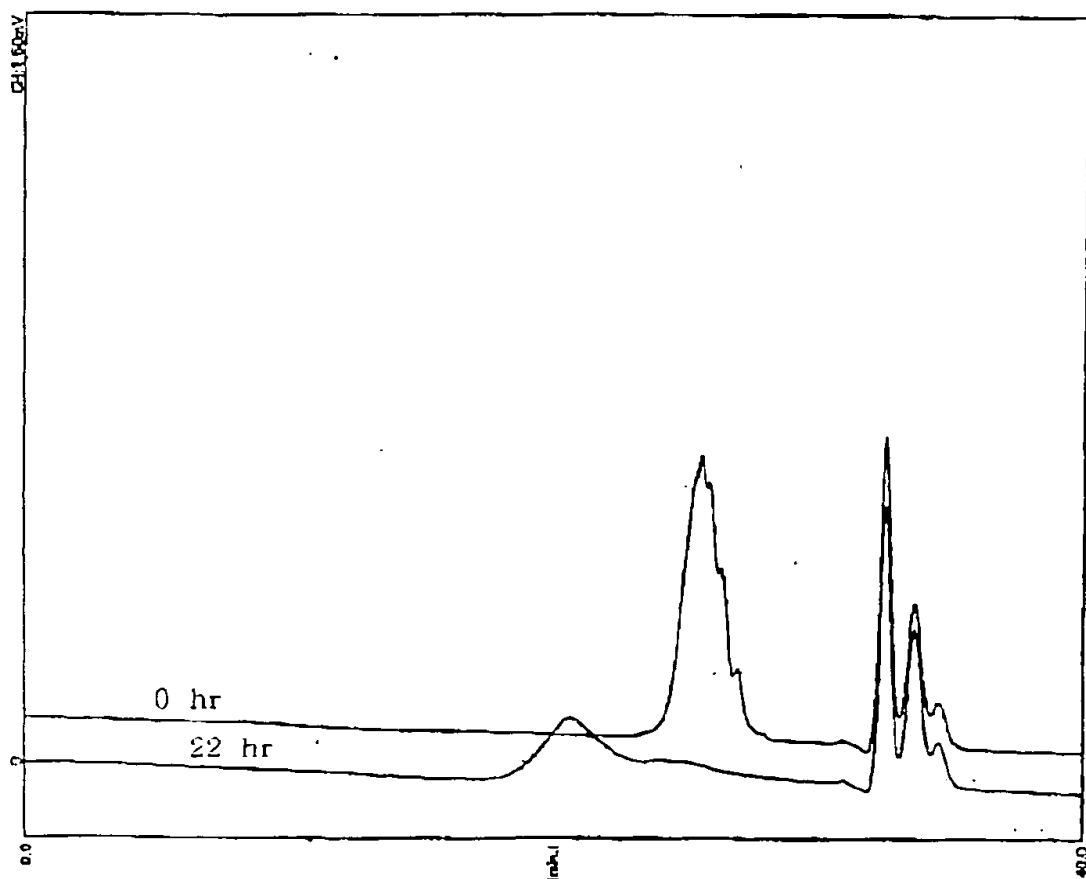


Figure 1

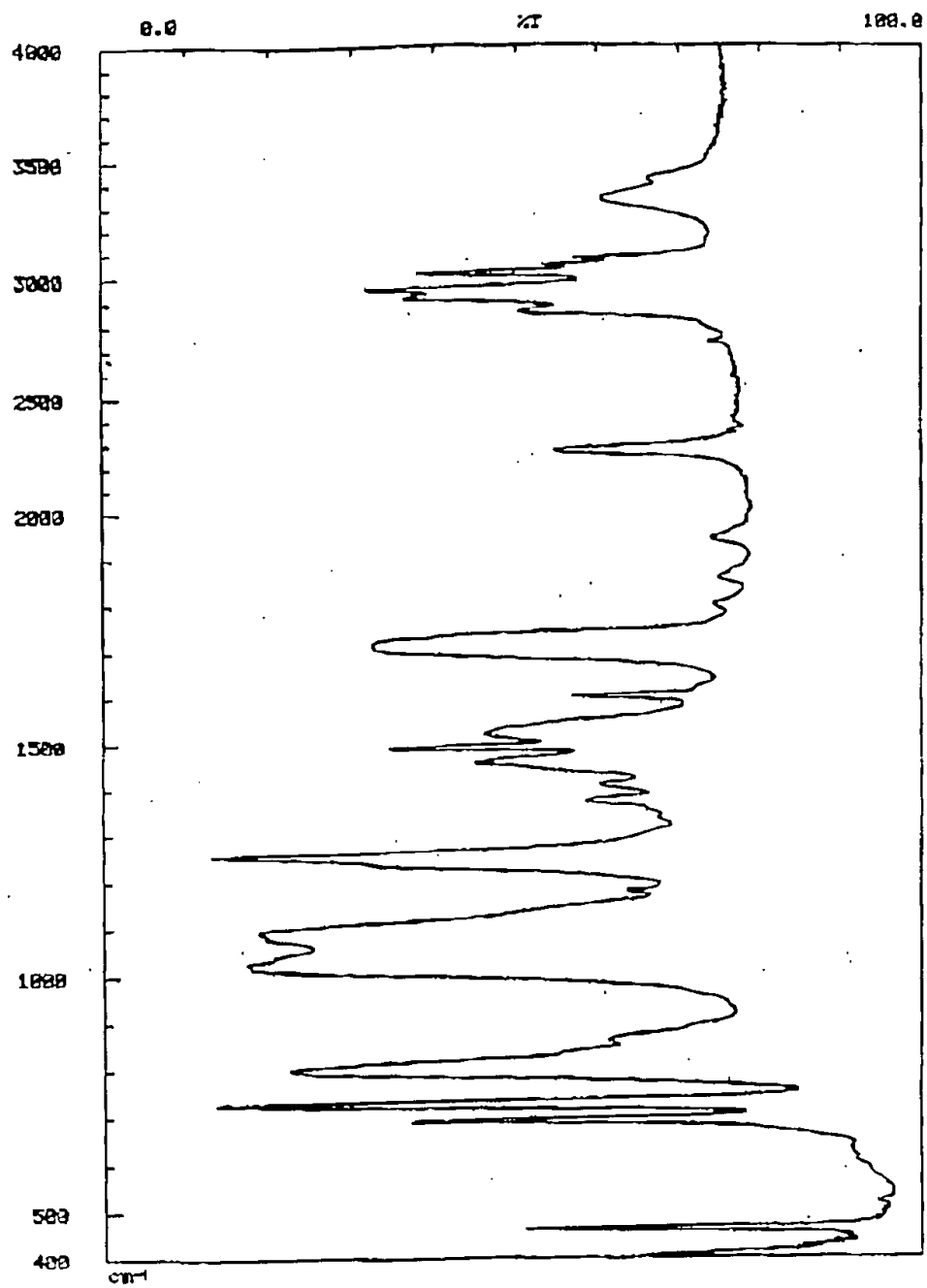


Figure 2

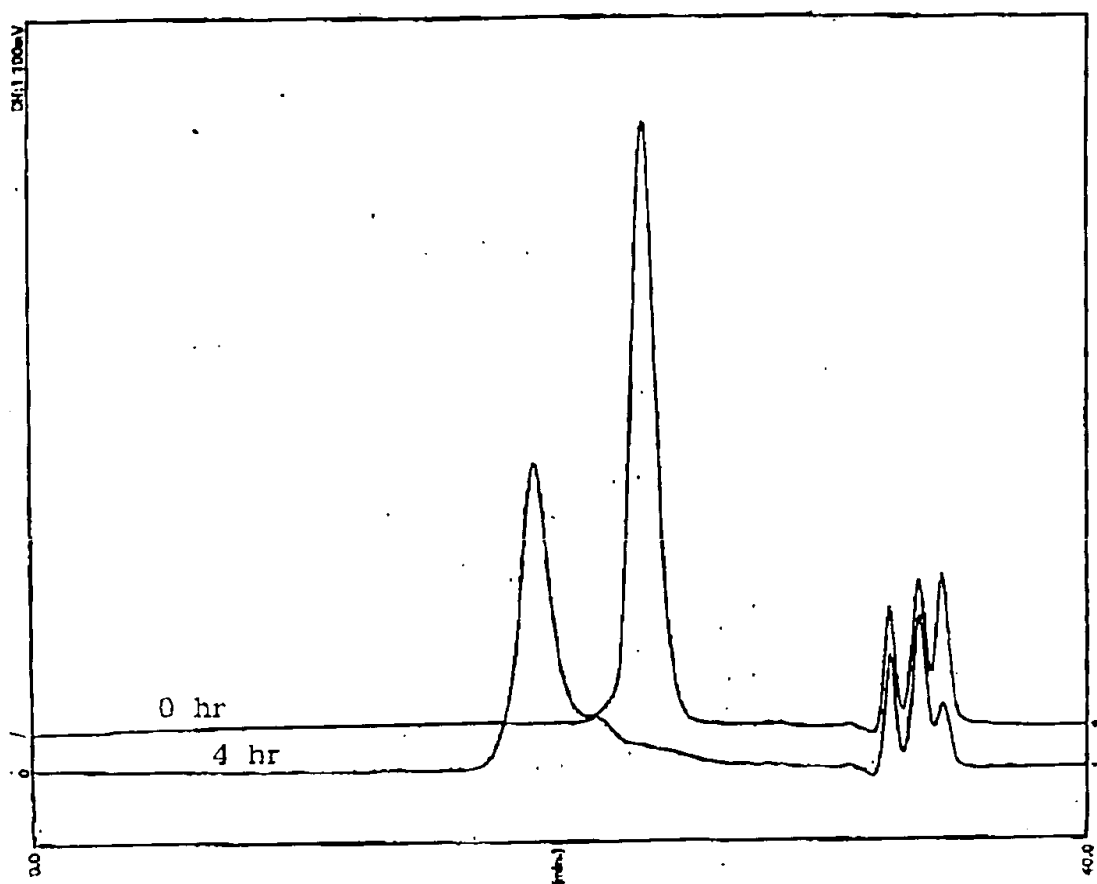


Figure 3

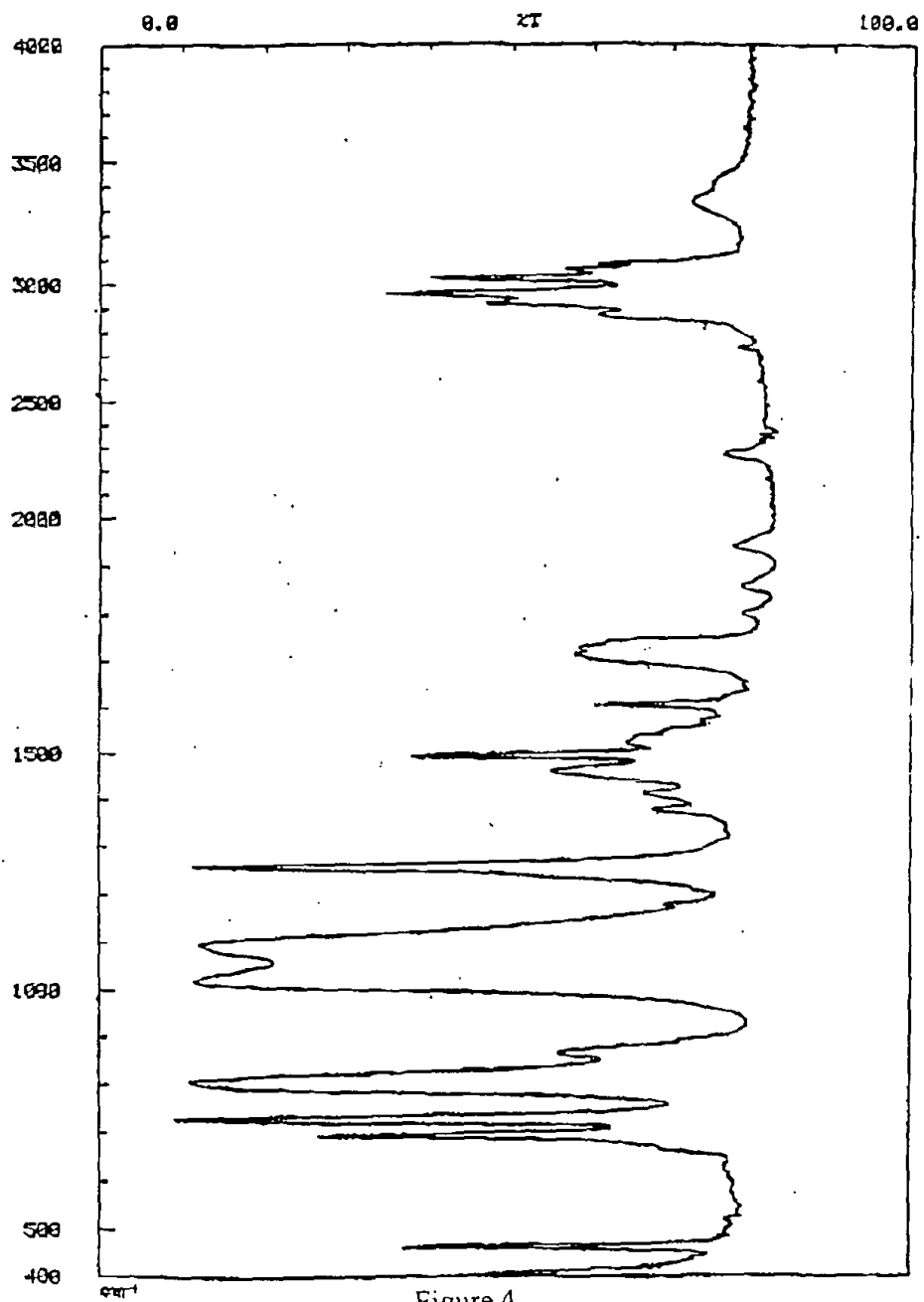


Figure 4

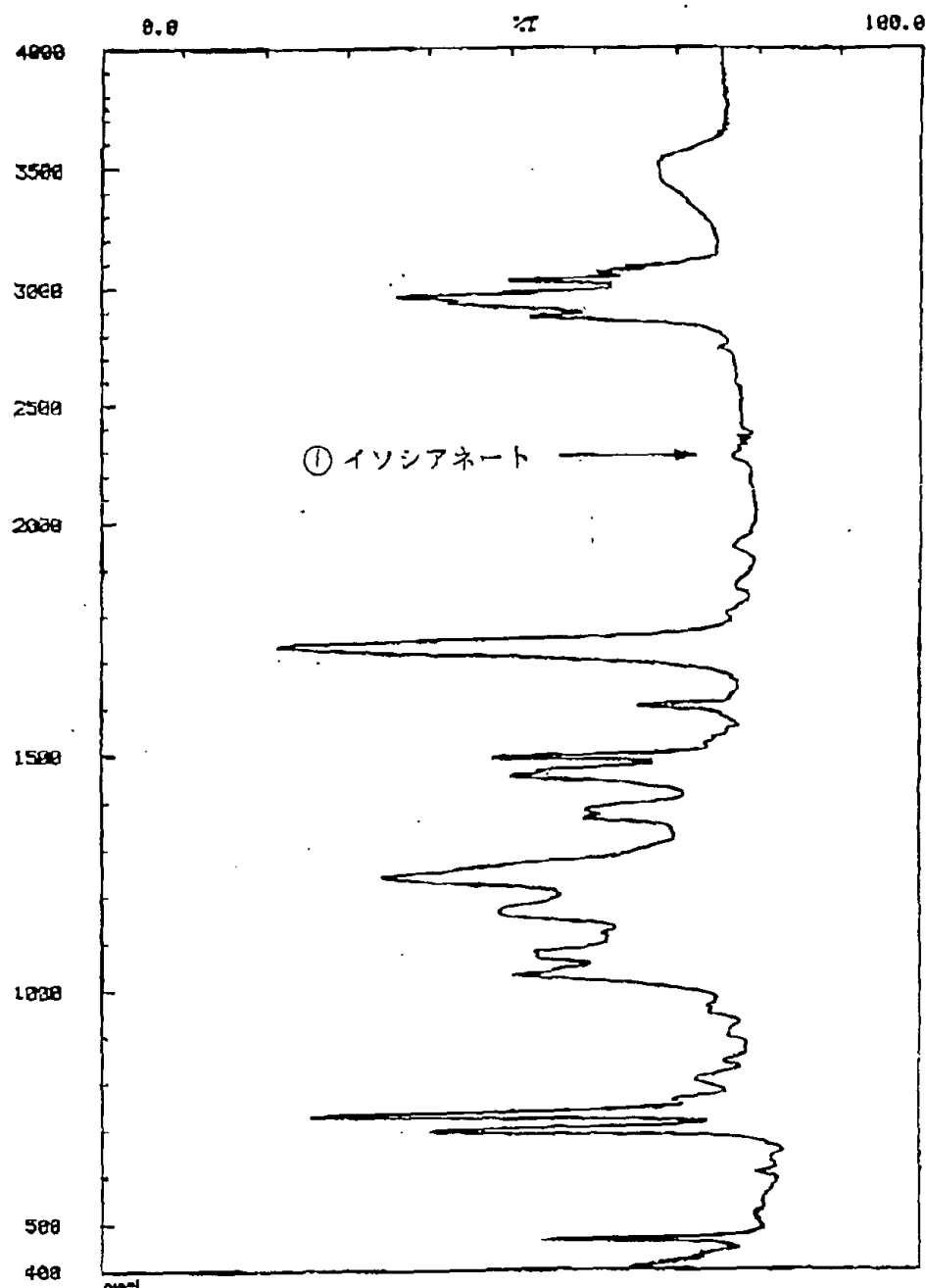


Figure 5

Key: 1 Isocyanate

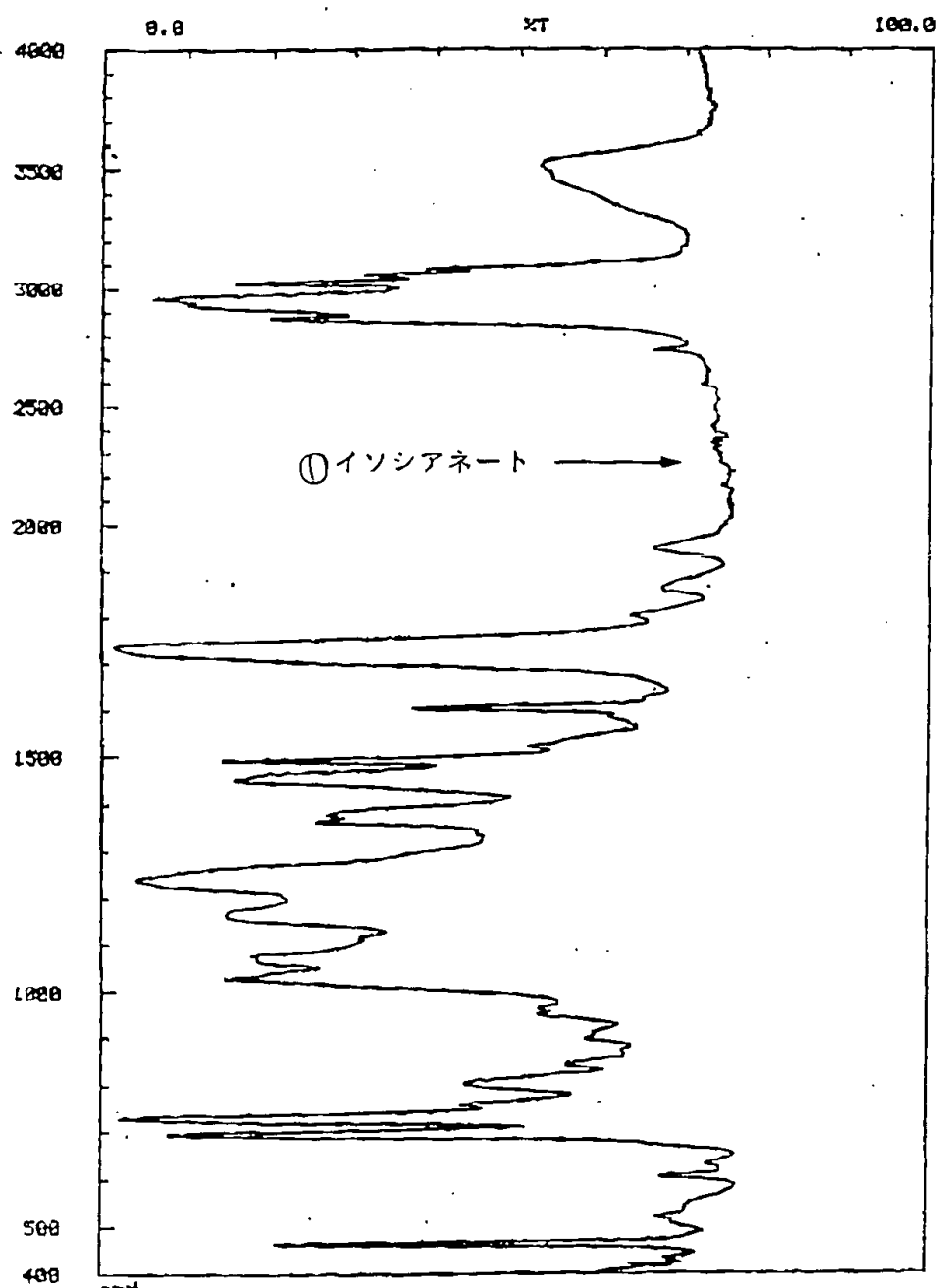


Figure 6

Key: 1 Isocyanate